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Quasi-1D in-plane order in Langmuir Monolayers of Fatty Acids on Liquid Mercury Surfaces

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Beamline(s): X22B

Introduction: The Ångström-scale structure of Langmuir monolayers (LMs) of long-chain fatty acids at the liquid mercury surface was recently studied at NSLS, using synchrotron x-ray methods[1]. The interplay between the van der Waals interchain interaction and the high chain-subphase attraction yields a sequence of novel 2D phases, where at low coverage the layer consists of a single or double layer of flat-lying molecules and at high coverages - of a monolayer of standing up molecules. These new phases provide new insight into fundamentals of the molecular-level interactions in general, and, in particular, those between organic and metallic molecules, which are of central importance for nanofabrication and bio-metallic interfacing[2].

Methods and Materials: All the fatty acids (C_nOOH, n=14,18 and 24) were purchased from Sigma or Fluka and marked as >99% pure. A Langmuir trough mounted on the liquid surface x-ray spectrometer at X22B, allowed simultaneous x-ray and surface tension measurements. Grazing incidence diffraction (GID) measurements were carried out on the flat-lying phases, to determine their in-plane structure. Bragg-rod scans (BRs), in which the intensity distribution along q_z (the surface-normal wavevector transfer component) is being measured at the GID peak, were also carried out.

Results: The single and the double layer phases of flat-lying molecules exhibit several low-$q_{||}$ GID peaks, $q_{||}$ being the surface-parallel wavevector transfer component. The GID peaks obtained for $C_{18}OOH$ are shown in the inset to Fig.1. All peak positions are multiples of $q_{||}$=0.12 Å^{-1}. The sharp peaks indicate a well-ordered structure with a repeat distance of 52.4 Å, larger by 3 Å than the corresponding 49.3 Å bulk layer spacing[3], where the layers consist of molecular dimers. This implies that our LM phase consists of uniform-width stripes of flat-lying dimers, oriented along the strip width. The BR results, shown in Fig.1 as a 3D pattern and as contour plots, are consistent with this conclusion. No clear strong peaks were observed at $q_{||}$=1.2-1.5 Å^{-1}, which would correspond to a lateral order with a repeat distance of the order of the molecular width, ~ 5Å. This suggests that along the stripes there is only short-range order, i.e. that the in-plane order is quasi-1D.

Conclusions: Rare flat-laying quasi-1D smectic-like LM phases were discovered. Further studies on other amphiphilic LMs on liquid metals may shed light on the possible conformational differences between the bulk and the LM molecules, which may be responsible for the different longitudinal repeat distances in the bulk and in the LM, and for the absence of lateral order, transverse to the long axis, in LMs.

References:

[1] H. Kraack *et al.*, *Annual Report*, NSLS (2001).
[2] A. Hatzor and P.S. Weiss, *Science* **291**, 1019 (2001); B. Kasemo, *Surf. Sci.* **500**, 656 (2002).
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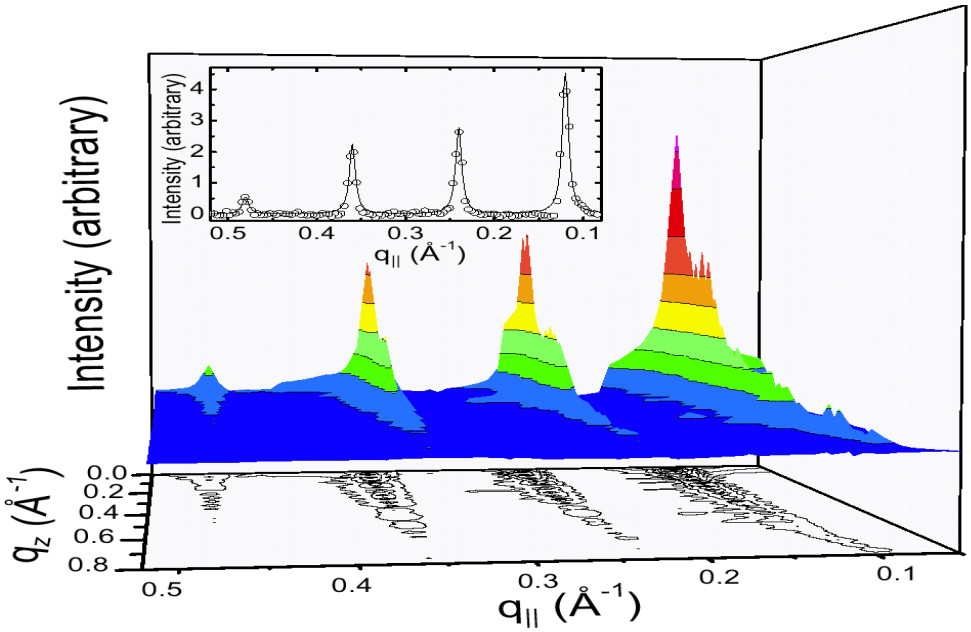

Fig.1: The measured ($q_{||}$,q_z) diffraction pattern for the flat-lying double-layer phase of $C_{18}OOH$ on mercury. A contour plot of the BRs is shown under the color-coded pattern. The GID scan is shown in the inset.